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On the raman spectra of monomeric vinyl acetate in liquid and solid states and infrared spectrum of the polymer

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The Raman spectrum of monomeric vinyl acetate solidified and cooled to −180°C has been recorded and compared with that of the liquid monomer. Infrared spectra of the monomer and polyvinyl acetate, probable assignments of some of the frequencies and a comparison with the Raman spectra of the monomer in the two states are given. Out of the 21 vibrational frequencies recorded in the present investigation the Raman line 243 cm^{-1}, probably due to the in-plane bending vibration of the C–C=O group, was not reported previously. Appreciable change in the frequencies of either the stretching or the deformation vibration of the monomer due to solidification could not be observed. Similarly, no low frequency Raman line appeared in the spectrum of the frozen monomer. Further, no appreciable change in frequencies due to the various deformation vibrations of vinyl acetate by polymerication of the molecules could be detected. However, persistence of a weak infrared band at 1637 cm^{-1} in the spectrum of the polyvinyl acetate indicates the possibility of formation in the polymer of rings in which C=C group reappears due to some internal condensation. These results indicate that probably intermolecular association does not take place in either frozen monomeric vinyl acetate or polyvinyl acetate, unlike as observed in cases of styrene, acrylonitrile and methacrylate but in conformity with the nature of the substituent in vinyl acetate molecule, namely, a group wihout any non-bonding electron pair or resonance stabilised structure.

1. Introduction

The Raman spectrum of monomeric vinyl acetate was studied by Taufen & Murray (1954) and by Simon *et al* (1958). The latter authors also studied the Raman spectrum of polyvinyl acetate and concluded that there was no intermolecular association in the polymer. Thomson & Torkington (1945) also did not mention about intermolecular assciation from their studies on the infrared spectra of vinyl acetate and polyvinyl acetate. Earlier studies by the author with monomers solidified, and cooled to −180°C revealed

evidence of formation of intermolecular association through weak electronic linkage in cases of methyl methacrylate (Roy 1953) styrene (Roy 1954) and acrylonitrile (Roy 1963) in frozen monomeric as well as in polymeric forms of these compounds. Hence, the study of Raman spectrum of monomeric vinylacetate solidified and cooled to $-180°$ was undertaken, and the spectrum was compared to that due to the monomer in liquid state atate at room temperature. The infrared spectra of the monomer and polymerised vinyl acetate were reinvestigated to find out whether changes in the spectrum which might be observed with the solidification of the monomer take place also with polymarisation. The results from these investigations are presented here.

2. Experimental

Vinyl acetate monomer was prepared from a sample of stablised vinyl acetate (National Chemical Laboratory, India) by removal of the stabiliser and purification of the monomer through distillation at highly reduced pressure and low temperature so that risk of polymerisation was negligible. Absence of the polymer in purified monomer was confirmed by the turbidity test with petroleum ether added to the monomer in acetone solution. The purified monomer was redistilled at low temperature under reduced pressure in pyrox glass double bulbs immediately before its spectra were recorded.

Sample of the polymer was prepared from commercial polymerised vinyl acetate (British Drug House Ltd., England) by cutting the commercial product into small pieces filling in a pyrox glass container and heating for 20 hours $120° \pm 1°C$ in a vacuum oven. For recording the infrared spectrum of the polymer thin films (less than 0.1 mm in thickness) were made through rolling the polymer between two glazed irons electrically heated to about 100°C. The film was kept under pressure in a paper frame to prevent shrinking.

The Raman spectra of the purified monomeric vinyl acetate in liquid state at room temperature and in solidified form at $-180°C$ were recoded by methods described earlier (Roy 1953) using a Fuess glass spectrograph having a dispersion of about 11.5 Å per mm at 4046 Å region. Iron are spectrum was photographed in each spectrum for comparison. After each exposure test for the detection of presence of any polymar in the monomer was applied, and spectrograms of samples showing no trace of polymer were studied only.

The infrared spectra of the purified monomeric and polymeric vinyl acetate were recorded with a Perkin-Elmer Model 21 spectrophotometer provided with rock salt optics. Thin film (0.022 mm) of the liquid obtained between two rock salt plates, and slightly thicker (less than 0.1 mm) film of the polymer prepared as described earlier were used to record infrared spectra.

3. Results and Discussion

The Raman shifts of the monometric vinyl acetate in the liquid and solid states, together with the frequencies of the infrared bands in the 620 to 2000 cm^{-1} region due to the monomeric liquid are given in table 1. Raman shifts of the liquid monomer reported by Simon *et al* (1958) are also given for comparison in this table. The frequencies of the infrared bands of polyvinyl acetate have been tabulated and a probable assignment of some of these frequencies are given in table 2. The Raman shifts due to the polymeric vinylacetate obtained by Simon *et al* (1958) are also included in table 2 for comparison.

Table 1. Raman shifts and Infrared frequencies of monomeric vinyl acetate

Infrared frequency" in cm^{-1} of the liquid monomer at 27°C (Present investigation)	Raman shifts" in cm^{-1}		
	Liquid Simon *et al* (1958)	Liquid at 30°C (Present investigation)	Solid at −180°C (Present investigation)
864 m	879(2sb)	243(1, b)	
	407(4)	407(8)	407(0)
	463(2)	461(4)	
	637(3vb)	635(6)	645(1)
	707(1, b)	700(1, b)	
842 m(h)	849(2, b)	842(2)	
864 m	879(2sb)	874(2)	
943 m	952(½)	952(0)	
970 w	977(2)	976(2)	
1010 s			
1130 vs	1139(2b)	1131(2)	
1205 vs			
1220(b)	1216(1vb)	1219(3vb)	
1292(m)	1295(8)	1296(15)	1292(3vb)
1365 s	1372(3)	1374(3)	1383(0b)
	1388(3)	1388(3)	
1422 w	1432(½ vsb)		
1645 s	1647(10)	1646(16)	1648(5)
1700 w			
1712 m			
1748 vs	1758(4)	1753(6)	1753(2b)
	2941(8)	2937(12)	2939(3)
	2998(3)	2990(4)	2992(1)
	3023(½)		
	3048(2)	3060(4)	3062(3)
	3094(1)	3102(0)	3102(0)
	3126(2)	3127(2)	3127(0)

It can be seen from table 1 that in the Raman spectrum of the liquid monomer only 21 vibrational frequencies out of the 30 expected modes of vibration for the molecule of vinyl acetate have been recorded.

Table 2. Infrared frequencies of polyvinyl acetate

Raman shifts in cm^{-1} Simon *et al* (1958)	Infrared frequencies in cm^{-1} polymer Present investigation	Probable Assignment
368 (0b)		
403 0b)		
462 (000)		
606 (00)		
632 (2)		
659 (0b)		
799 ($\frac{1}{2}$)	792 m	CH_2 rock to polymer chain axis
847 (0)	845 vw	
882 ($\frac{1}{2}$b)	895 m (h)	
909 (000)		
942 (00)	943 (s)	
975 (00)	980 m(h)	
1024 ($\frac{1}{2}$)	1018 vs	-C-C-C skeleton vibration
1136 ($\frac{1}{2}$b)	1120 s (flat plateau)	C CH_2 rock
1174		
1227 (000)	1220 vs	C – O – C bend
1256 (000)	1240 vs	
1295 ($\frac{1}{2}$)	1262 vs	CH wag
1354 (1b)	1362 vs	Symmetric CH bend of CH_3
1379 (1b)	1378 vs	
1439 (3)	1425 vw	Antisymmetric CH bend of CH_3
	1435 s	CH_3 scissoring
1647 (1)	1560 w	
	1637 m (h)	C = C stretch
	1700 m	
	1710 vs (h)	
	1725 bs	C = O stretch
1738 (3vv)	1738 vs	
	1750 vs	
	1820 w	
2870 (1)		
2930 (3)		
2939 (4)		
2988 ($\frac{1}{2}$)		
3022 ($\frac{1}{2}$)		
3091 (0b)		

A Raman line 243 cm^{-1} not reported by either Taufen & Murray (1954) or Simon *et al* (1958) has been observed. This line may be due to the in-plane bending vibration of the C—C=O group. The Raman lines 1646 and 1753 cm^{-1} of the monomer are easily assigned to the stretching vibrations of the C = C and C = O bonds respectively. The intensites of these two lines are reversed in the infrared spectra of the monomer. Unlike as in the case of methyl methacrylate (Roy, 1953), the intensity of the line 1646 cm^{-1} relative to that of the line 1753 cm^{-1} does not undergo any change with the solidification of the monomer. No other appreciable change is observed in the frequencies of either the stretching or the deformation vibrations of the monomer with solidification. Moreover, no low frequency Raman line has appeared in the spectrum of the frozen monomeric vinyl acetate, as was observed in cases of methyl methacrylate (Roy, 1953), styrene (Roy, 1954) and acrylonitrile (Roy, 1963). These results indicate that there is hardly any intermolecular association in the frozen monomeric vinyl acetate.

From a comparison of the infrared bands due to monomer and polymer, tables 1 and 2 respectively, it can be seen that the frequencies due to the various deformation vibration of vinyl acetate do not undergo appreciable change on polymerisation, unlike as was observed in case of acrylonitrile (Roy, 1963). For example, the infrared bands at 1220, 1365 and 1422 cm^{-1} of the monomer due respectively to the C-O-C bend, the symmetric C-H bend and the antisymmetric C-H bend of CH_3 appear at 1220, 1362 and 1425 cm^{-1} in the spectrum of the polymer. These results indicate that probably intermolecular association does not take place in the polymer molecules also.

As in the case of polyacrylinitrile (Roy, 1963) a weak infrared band at 1637 Cm^{-1}, probably representing C = C stretching vibration, is observed in the spectrum of the polymer. Thomson & Torkington (1954) reported an infrared band at about 1930 cm^{-1} due to the polymer, while Simon *et al* (1958) observed a feeble Raman line at 1647 cm^{-1} in the spectrum of a carefully purified sample of polyvinyl acetate. These authors could not explain away the above mentioned frequency as originating from the presence of monomer included in the polymer. The former authors made the reservation that this frequency may also be due to some unexpected types of condensation, while the latter authors concluded that terminal double bonds were involved to give the frequency. The existence of unsaturation in the terminal groups of the polyvinyl chains has been proved by chemical investigations (Marvel & Inskeep, 1943). The chain length and, in consequence, the number of structural units polyvinyl acetate prepared by bulk polymerisation is not very large. Hence, the proportion of the terminal double bonds to the total number of structural units is not too insignificant as in the case of polyacrytonitrile, and this fact may probably explain the persistance of the weak band 1637 cm^{-1} in this infrared spectrum of the polymer. But, even then, the intensity of this band is somewhat greater than would be expected from the above consideration,

and hence the possibility of formation of rings in which C = C group reappears due to some internal condensation, as occurs in the case of polymethyl vinyl Ketone (Marvel & Levesque, 1938), cannot be ruled out.

The absence of intermolecular association in the case of frozen vinyl acetate monomer, as inferred from the present investigation, contrary to the presence of the same in frozen styrene and acrytonitrile and to a less extent in frozen methyl methacrylate, is significant. These results lead to conclude upon the nature of the substituent groups in vinylic monomer which may favour the formation of intermolecular association through weak electronic linkage in the frozen state of the monomers, and probably in the polymers also. In case the substituent group in the vinylic monomer has either non-bonding electrons, as in acrylonitrile (Roy, 1963) or a resonance stabilised radical, as in styrene (Roy, 1954) and methyl methacrylate (Roy, 1953), intermolecular association is to be found. But in absence of any such substituent group, as in vinyl acetate, it is likely that there is hardly any intermolecular association in the solidified monomer, or in the polymer.

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